VOLATILE ORGANIC COMPOUNDS (VOCs) in Ambient Air Using Summa Canister Sampling and Gas Chromatography (GC) Analysis

EPA Method TO-14

Table 1A. Summary of Holding Times and Preservation for Volatile Organic Compounds (VOCs) in Ambient Air

| Analytical Parameter a | Technical and Contract Holding Times | Preservation |
|--|--|--|
| Volatile Organic Compounds (VOCs) in SUMMA® canisters ^b | Technical: 14 days from collection; Contract: 12 days from receipt at laboratory | Ambient temperature; at or near atmospheric pressure |
| VOCs in tedlar bags | Technical: 48 hours from collection; Contract: 36 hours from receipt at laboratory | Ambient temperature; at or near atmospheric pressure |

a Individual target compounds are listed in Table 1B.

Data Calculations and Reporting Units:

Calculate and report the sample results as specified in the EPA Method TO-14. All records of analyses, dilutions and calculations must be legible and sufficient to recalculate all sample concentrations and QC results.

Perform sample quantitation using the response factor (RF) from the average response factors of the calibrated range. Report results for all target analytes in concentration units of parts per billion by volume (ppbv).

Report tentatively identified compounds (TICs) with a response of <10% of the nearest internal standard. TIC values should be estimated in ppbv based on the response of the corresponding internal standard.

For rounding results, adhere to the following rules:
a)If the number following those to be retained is less than 5, round down;
b)If the number following those to be retained is greater than 5, round up; or
c)If the number following the last digit to be retained is equal to 5, round
down if the digit is even, or round up if the digit is odd.

All records of analysis and calculations must be legible and sufficient to recalculate all sample concentrations and QC results. Include an example calculation in the data package.

b The laboratory must provide clean and certified 6-liter SUMMA® canisters with the manufacturer's serial number, or a unique permanent identification number attached. For cleaning and certification of SUMMA® canisters, follow the requirements specified in Sections 7.3 and 11 of EPA Method TO-14. After cleaning and certification, the SUMMA canisters will be shipped to the field with a vacuum of < 50 mm TORR. One canister shall be designated as the trip blank for each SDG.

Table 1B. Target Compound List and Contract Required Quantitation Limits for VOCs by EPA Method TO-14

| Acetonitrile 5 Acrolein 5 Acrylonitrile 5 Benzene 2 Benzyl chloride 5 Bromodichloromethane 2 Bromomethane 5 1,3-Butadiene 5 2-Butanone 5 Carbon tetrachloride 2 Chlorobenzene 2 Chlorodifluoromethane 2 Chloroethane 2 Chloroform 2 Chloromethane 2 3-Chloro-1-propene 2 Cyclohexane 2 Dibromochloromethane 2 1,2-Dibromoethane 2 1,2-Dichlorobenzene 5 1,4-Dichlorobenzene 5 Dichlorodifluoromethane 2 1,1-Dichlorobenzene 5 Dichlorodifluoromethane 2 | obv) |
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| Acrolein 5 Acrylonitrile 5 Benzene 2 Benzyl chloride 5 Bromodichloromethane 2 Bromomethane 5 1,3-Butadiene 5 2-Butanone 5 Carbon tetrachloride 2 Chlorobenzene 2 Chlorodifluoromethane 2 Chlorothane 2 Chlorothane 2 Chlorothane 2 Chloromethane 2 Chloromethane 2 Chloromethane 2 1,2-Dibromoethane 2 1,2-Dibromoethane 2 1,2-Dichlorobenzene 5 1,4-Dichlorobenzene 5 Dichlorodifluoromethane 5 Dichlorodifluoromethane 5 Dichlorodifluoromethane 5 Dichlorodifluoromethane 5 Dichlorobenzene 5 Dichlorodifluoromethane 5 | |
| Acrylonitrile 5 Benzene 2 Benzyl chloride 5 Bromodichloromethane 2 Bromomethane 5 1,3-Butadiene 5 2-Butanone 5 Carbon tetrachloride 2 Chlorobenzene 2 Chlorodifluoromethane 2 Chloroethane 2 Chloroethane 2 Chloromethane 2 Chloromethane 2 Chloromethane 2 1,2-Dibromoethane 2 1,2-Dibromoethane 2 1,2-Dichlorobenzene 5 1,4-Dichlorobenzene 5 Dichlorodifluoromethane 5 Dichlorodifluoromethane 5 Dichlorobenzene 5 Dichlorodifluoromethane 5 | |
| Benzene 2 Benzyl chloride 5 Bromodichloromethane 2 Bromomethane 5 1,3-Butadiene 5 2-Butanone 5 Carbon tetrachloride 2 Chlorobenzene 2 Chlorodifluoromethane 2 Chlorodethane 2 Chloroform 2 Chloromethane 2 Chloromethane 2 Chloromethane 2 1,2-Dibromoethane 2 1,2-Dibromoethane 2 1,2-Dichlorobenzene 2 1,3-Dichlorobenzene 5 1,4-Dichlorobenzene 5 Dichlorodifluoromethane 5 | |
| Benzyl chloride 5 Bromodichloromethane 2 Bromomethane 5 1,3-Butadiene 5 2-Butanone 5 Carbon tetrachloride 2 Chlorobenzene 2 Chlorodifluoromethane 2 Chlorodifluoromethane 2 Chloroform 2 Chloroform 2 Chloronethane 2 3-Chloro-1-propene 2 Cyclohexane 2 Dibromochloromethane 2 1,2-Dichlorobenzene 2 1,3-Dichlorobenzene 5 1,4-Dichlorobenzene 5 Dichlorodifluoromethane 2 | |
| Bromodichloromethane 5 Bromomethane 5 1,3-Butadiene 5 2-Butanone 5 Carbon tetrachloride 2 Chlorobenzene 2 Chlorodifluoromethane 2 Chloroethane 2 Chloroform 2 Chloromethane 2 3-Chloro-1-propene 2 Cyclohexane 2 Dibromochloromethane 2 1,2-Dichlorobenzene 2 1,3-Dichlorobenzene 5 1,4-Dichlorobenzene 5 Dichlorodifluoromethane 2 Dichlorodifluoromethane 5 Dichlorodifluoromethane 5 | |
| Bromomethane 5 1,3-Butadiene 5 2-Butanone 5 Carbon tetrachloride 2 Chlorobenzene 2 Chlorodifluoromethane 2 Chloroethane 2 Chloroform 2 Chloromethane 2 3-Chloro-1-propene 2 Cyclohexane 2 Dibromochloromethane 2 1,2-Dibromoethane 2 1,2-Dichlorobenzene 5 1,4-Dichlorobenzene 5 Dichlorodifluoromethane 2 Dichlorodifluoromethane 5 | |
| 1,3-Butadiene 5 2-Butanone 5 Carbon tetrachloride 2 Chlorobenzene 2 Chlorodifluoromethane 2 Chloroethane 2 Chloroform 2 Chloromethane 2 3-Chloro-1-propene 2 Cyclohexane 2 Dibromochloromethane 2 1,2-Dichlorobenzene 2 1,3-Dichlorobenzene 5 1,4-Dichlorobenzene 5 Dichlorodifluoromethane 2 | |
| 2-Butanone 5 Carbon tetrachloride 2 Chlorobenzene 2 Chlorodifluoromethane 2 Chloroethane 2 Chloroform 2 Chloromethane 2 Chloromethane 2 Chloromethane 2 I,2-Dibromoethane 2 I,2-Dibromoethane 2 I,2-Dichlorobenzene 5 I,4-Dichlorobenzene 5 Dichlorodifluoromethane 2 | |
| Carbon tetrachloride 2 Chlorobenzene 2 Chlorodifluoromethane 2 Chloroethane 2 Chloroform 2 Chloromethane 2 Chloromethane 2 Chloromethane 2 3-Chloro-1-propene 2 Cyclohexane 2 Dibromochloromethane 2 1,2-Dibromoethane 2 1,2-Dichlorobenzene 5 1,4-Dichlorobenzene 5 Dichlorodifluoromethane 2 | |
| Chlorobenzene 2 Chlorodifluoromethane 2 Chloroethane 2 Chloroform 2 Chloromethane 2 Chloromethane 2 Chloromethane 2 3-Chloro-1-propene 2 Cyclohexane 2 Dibromochloromethane 2 1,2-Dibromoethane 2 1,2-Dichlorobenzene 2 1,3-Dichlorobenzene 5 1,4-Dichlorobenzene 5 Dichlorodifluoromethane 2 | |
| Chlorodifluoromethane 2 Chloroethane 2 Chloroform 2 Chloromethane 2 Chloromethane 2 3-Chloro-1-propene 2 Cyclohexane 2 Dibromochloromethane 2 1,2-Dibromoethane 2 1,2-Dichlorobenzene 2 1,3-Dichlorobenzene 5 1,4-Dichlorobenzene 5 Dichlorodifluoromethane 2 | |
| Chloroethane 2 Chloroform 2 Chloromethane 2 3-Chloro-1-propene 2 Cyclohexane 2 Dibromochloromethane 2 1,2-Dibromoethane 2 1,2-Dichlorobenzene 2 1,3-Dichlorobenzene 5 1,4-Dichlorobenzene 5 Dichlorodifluoromethane 2 | |
| Chloroform 2 Chloromethane 2 3-Chloro-1-propene 2 Cyclohexane 2 Dibromochloromethane 2 1,2-Dibromoethane 2 1,2-Dichlorobenzene 2 1,3-Dichlorobenzene 5 1,4-Dichlorobenzene 5 Dichlorodifluoromethane 2 | |
| Chloromethane 2 3-Chloro-1-propene 2 Cyclohexane 2 Dibromochloromethane 2 1,2-Dibromoethane 2 1,2-Dichlorobenzene 2 1,3-Dichlorobenzene 5 1,4-Dichlorobenzene 5 Dichlorodifluoromethane 2 | |
| 3-Chloro-1-propene 2 Cyclohexane 2 Dibromochloromethane 2 1,2-Dibromoethane 2 1,2-Dichlorobenzene 2 1,3-Dichlorobenzene 5 1,4-Dichlorobenzene 5 Dichlorodifluoromethane 2 | |
| Cyclohexane 2 Dibromochloromethane 2 1,2-Dibromoethane 2 1,2-Dichlorobenzene 2 1,3-Dichlorobenzene 5 1,4-Dichlorobenzene 5 Dichlorodifluoromethane 2 | |
| Dibromochloromethane 2 1,2-Dibromoethane 2 1,2-Dichlorobenzene 2 1,3-Dichlorobenzene 5 1,4-Dichlorobenzene 5 Dichlorodifluoromethane 2 | |
| 1,2-Dibromoethane21,2-Dichlorobenzene21,3-Dichlorobenzene51,4-Dichlorobenzene5Dichlorodifluoromethane2 | |
| 1,2-Dichlorobenzene21,3-Dichlorobenzene51,4-Dichlorobenzene5Dichlorodifluoromethane2 | |
| 1,3-Dichlorobenzene51,4-Dichlorobenzene5Dichlorodifluoromethane2 | |
| 1,4-Dichlorobenzene 5 Dichlorodifluoromethane 2 | |
| Dichlorodifluoromethane 2 | |
| | |
| 1,1-Dichloroethane 2 | |
| | |
| 1,2-Dichloroethane 2 | |
| 1,1-Dichloroethene 5 | |
| cis-1,2-Dichloroethene 2 | |
| trans-1,2-Dichloroethene 2 | |
| 1,2-Dichloropropane 2 | |

| Dichlorofluoromethane | 2 |
|---|---|
| t-1,2-Dichloropropene | 2 |
| cis-1,2-Dichloropropene | 5 |
| 1,2-Dichloro-1,1,2,2-tetra-fluoroethane | 2 |
| Ethylbenzene | 2 |
| Heptane | 2 |
| Hexachlorobutadiene | 5 |
| Hexane | 2 |
| Methanol | 5 |
| Methylene chloride | 5 |
| Methyl methacrylate | 2 |
| 4-Methyl-2-pentanone | 5 |
| alpha-Methyl styrene | 5 |
| Octane | 5 |
| n-Pentane | 2 |
| Propylene | 5 |
| Styrene | 5 |
| 1,2,4-Trichlorobenzene | 2 |
| 1,1,1-Trichloroethane | 5 |
| 1,1,2-Trichloroethane | 5 |
| 1,1,2,2-Tetrachloroethane | 2 |
| Tetrachloroethene | 5 |
| Toluene | 5 |
| Trichloroethene | 2 |
| Trichlorofluoromethane | 2 |
| 1,1,2-Trichloro-1,2,2-trifluoroethane | 2 |
| 1,2,4-Trimethylbenzene | 2 |
| 1,3,5-Trimethylbenzene | 2 |
| Vinyl acetate | 5 |
| Trimal ablaction | 2 |
| Vinyl chloride | |
| Xylenes (m- and p-) | 5 |
| | |

Table 2. Summary of Calibration Procedures for VOCs by EPA Method TO-14

| Calibration Element | Frequency | Acceptance Criteria | Corrective Action |
|--|--|--|--|
| GC/MS Tuning with 4- bromofluorobenzene (BFB) | Beginning of each 12 hour period during which standards and samples are analyzed | Ion abundance criteria in Table 4 of Method TO- 14 | Identify the problem. MS tune criteria must be met before calibration |
| Initial Calibration (minimum blank + 3 to 5 points for each analyte) (ICAL) a, b, c | Initially; whenever required, due to failure of CCV | RSD for RFs #25% | 1. Terminate analysis 2. Recalibrate and verify before sample analysis |
| Continuing Calibration Verification (CCV) (middle of the calibration range) | Following ICV, after every 10 samples, and end of run | %D between RF of CCV and avg. RRFs from ICAL #25% | 1. Recalibrate and verify 2. Reanalyze samples back to last good CCV |

^a The ICAL low standard must be at concentrations equivalent to the CRQL.

Follow the tuning and calibration procedures in Section 10.2.2 and 10.2.3 of EPA Method TO-14 and in SOP #1705, Section 3.7.1 and 3.7.2 of OSWER Directive 9360.4-05, May 1992.

The standards must be traceable to a known certified source.

b ICAL and CCV standards must contain all target analytes listed in Table 1B.

 $^{^{\}rm c}$ Report the retention time (RT) window for each analyte. Determine RT windows as ± 3 x the standard deviation (SD) of the average initial calibration RT for each analyte.

Table 3. Summary of Internal Quality Control Procedures for VOCs by EPA Method TO-14

| QC Element | Frequency | Acceptance Criteria | Corrective Action |
|--|--|---|--|
| Method Blank (MB) | One for each day, minimum of one per SDG ^a | < CRQL for each compound | 1. Investigate the source of contamination and document. 2. Reanalyze all samples processed with a blank that is out of control. |
| Performance Evaluation (PE) sample b | One per day or for each SDG batch | 80-120% of expected value | 1. Reanalyze all samples associated with a non-compliant PE sample. |
| Surrogate Spikes ^c | Every sample, standard and method blank | 70-130% of expected value | 1. Reanalyze all samples with non-compliant surrogate recoveries. |
| Laboratory Duplicates | One of every 10 samples or one per day, whichever is greater | RPD #20 between duplicate results \$5 times CRQL; ±CRQL for duplicate results #5 times CRQL | 1. Reanalyze all samples with non-compliant results. |

^a SDG - Sample Delivery Group - each case of field samples received; or each 20 field samples within a case; or each 14 calendar day period during which field samples in a case are received.

Dilute and reanalyze samples which contain one or more target analytes at concentrations above the initial calibration range. Results for such reanalyses should fall within the mid-range of the calibration curve. Report results and submit documentation for both analyses.

^b PE samples - The National Institute of Standards and Technology (NIST) standard reference materials (SRM) that are traceable to known concentrations.

 $^{^{\}mathrm{c}}$ Surrogates - The laboratory must demonstrate that the selected three surrogates do not interfere with any target analytes.